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PROCESS FOR MAKING A MONOFILAMENT-LIKE PRODUCT

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The invention relates to a process for making a monofilament-like product from a precursor containing at least one strand of polyolefin fibres, comprising the steps of a) exposing the precursor to a temperature within the melting point range of the polyolefin for a time sufficient to at least partly fuse adjacent fibres and b)

10 simultaneously stretching the precursor at a draw ratio of at least 1.0. The invention further relates to a monofilament-like product obtainable by said process, and to the use of said monofilament-like product for making various semi-finished and end-use products.

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Such a process is known from EP 0740002 B1. In this patent publication a process for making a fishing line from yarns of filamentous materials is described, wherein a braided, twisted, or twisted and plied fishing line made from yarns of gel spun polyolefin filaments, is exposed to a temperature within the melting point range of said polyolefin for a time sufficient to at least partially fuse adjacent filaments while stretching said line at a stretching ratio within the range from 1.01 to 2.5. The

20 yarns applied in this process are continuous multi-filament yarns, more specifically such yarns made by so-called gel spinning of ultra-high molar mass polyethylene (UHMWPE), for example yarns commercially available under the names Spectra® or Dyneema®.

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Fishing lines are generally monofilaments made from synthetic polymers, having a round, firm structure that allows convenient handling for bait casting, spinning, and spin casting. Such monofilament lines generally have a stiff nature and smooth surface, which combine to reduce drag during the cast and enable longer casts while providing better release from fishing reels. Braided lines are less suited for fishing lines, because they have a tendency to fray at the end of the line, may

30 entrap water, present an outer surface that is vulnerable to snags and entanglement, and have an opaque white colour which is too visible below water. The process known from EP 0740002 B1 allows making monofilament-like fishing lines from braided or twisted lines made from polyolefin multi-filaments yarns, which lines do not have the said disadvantages of braided lines.

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A disadvantage of the process described in EP 0740002 B1 is that the product obtained therewith shows limited resistance to break when exposed to abrasive conditions.

It is therefore an object of the present invention to provide a process for making a monofilament-like product that does not show said disadvantage.

This object is achieved according to the invention with a process for making a monofilament-like product from a precursor containing at least one strand of polyolefin fibres, comprising the steps of a) exposing the precursor to a temperature within the melting point range of the polyolefin for a time sufficient to at least partly fuse adjacent fibres and b) simultaneously stretching the precursor at a draw ratio of at least 1.0, wherein the strand is a spun yarn made from polyolefin staple fibres.

With the process according to the invention a monofilament-like product can be made from e.g. a plied or braided polyolefin yarn construction, which product shows improved abrasion resistance, as expressed in the number of cycles until break as measured in a test described under Materials and Methods.

The monofilament-like product obtained by the process according to the invention also shows surprisingly high tensile strength, significantly higher than the initial spun yarn or the plied yarn made from such spun yarn and used as the precursor. The mono-filament-like product obtained further has a pleasant touch or feel and can be easily handled and knotted; furthermore it shows surprisingly high knot strength and knot strength efficiency. Another advantage of the process according to the invention is that the degree of fusion can be easily varied and controlled; resulting in products with tailored property profiles. A still further advantage is that the monofilament-like product obtained may be effectively coated with a coating composition in an additional process step.

With the process according to the invention a monofilament-like product is made from a precursor containing at least one strand of polyolefin fibres. A monofilament-like product is understood to be a product that has an appearance and feel more resembling that of a monofilament than that of multi-filament yarn or cord, but which actually is made from at least one strand containing a multitude of fibres, which fibres typically have a diameter of less than about 50 micrometer.

The monofilament-like product may have a diameter that varies within a wide range, e.g from about 0.1 up to 10 millimetre. A precursor is herein understood to be an article of indefinite length that contains at least one strand of polyolefin fibres, and is used as feed or starting material. A suitable precursor can be in the form of for example a braided cord, a plied and twisted yarn, cord or rope comprising a number of strands, but also a single-strand yarn. A strand of polyolefin fibres is understood to be a fibrous

article like a yarn containing predominantly, i.e. 50 or more mass% of polyolefin fibres.

The process according to the invention comprises the step of exposing the precursor to a temperature within the melting point range of the polyolefin for a time sufficient to at least partly fuse adjacent fibres. The conditions of this fusion
5 step are chosen such, that the temperature and time of exposure are sufficient to soften the polyolefin fibres and to allow them to fuse at least partly within the specific structure applied. The melting point range of the polyolefin is the temperature range between the peak melting point of a non-oriented polyolefin and the peak melting point of a constrained highly-oriented polyolefin fibre, as determined by DSC analysis using
10 a scan-rate of 20°C/min. For UHMwPE fibres, typically showing a melting point range of 138-162°C, the temperature is preferably within the range from about 150°C up to about 157°C. Residence times during which the precursor is exposed to the fusion temperature may vary within a broad range, but are typically within the range from about 5 seconds to about 1500 seconds. Although higher temperatures tend to
15 enhance the fusion process, care should be taken not to apply too high a temperature as this may cause loss in strength of the product, resulting from e.g. partial melting or other molecular relaxation effects.

During the fusion process, the appearance of the precursor changes from an initial, opaque white colour into a translucent, milky, or even substantially
20 transparent surface appearance of the product, depending on the degree of fusion and type of precursor material. The light transmission of the product increases with increased degree of fusion between fibres. Such an increase in translucency or light transmission is a definite advantage for application as underwater fishing lines.

For a monofilament-like product showing low end fraying it suffices
25 that the outer surface layer of fibres is at least partly fused, as seen by increase in light transmission. A higher degree of fusion, e.g. also binding fibres in more inner parts of a precursor or strand, however, is preferred for making a product with higher abrasion resistance, and a higher bending stiffness, that is with more monofilament-like characteristics. The degree of fusion can be adjusted by varying exposure temperature
30 and/or time of exposure in the process according to the invention.

The degree of fusion can be determined on the product obtained, for example by visual evaluation, e.g. with the naked eye or by using an optical or electron microscope; or by measuring mechanical properties like strength or stiffness. Another possibility is to determine the amount and rate of absorption of a coloured liquid, e.g.

from a marker, as described in EP 0740002 B1. The degree of fusion can also be derived from a test, wherein the loaded product is abraded over a metal rod and the number of movements is determined after which the monofilament-like product disintegrates into its constituting filaments.

5 In a special embodiment of the process, the degree of fusion is only very low, or even hardly measurable on the product obtained. Surprisingly, it has been found that such product that has been stretched at elevated temperature does show markedly improved tensile strength over its precursor; be it that the abrasion resistance is only slightly better. The invention therefore also relates to a process for stretching a
10 braided or plied construction containing at least one strand of spun yarn made from polyolefin staple fibres at a draw ratio of at least 1.1, while exposing it to a temperature within the melting point range of the polyolefin. The product obtained with this process shows improved tensile properties, but still has bending properties much like the starting construction.

15 The process according to the invention also includes simultaneously stretching the precursor at a draw ratio, also called stretch ratio, of at least 1.0. Applying a draw ratio of at least 1 to the precursor during the heat exposure prevents a decrease in strength of the product. A draw ratio of 1.1 or higher tends to improve especially the tensile strength. The strength of the product is then surprisingly found to
20 be significantly higher than that of the precursor or of the strands contained therein. Above a certain draw ratio this effect levels off, or strength may even decrease as result of partly damaging or breaking of fibres. In addition, the higher the draw ratio, the lower the titre of the resulting product. The maximum draw ratio is thus dependent on the type of precursor and its fibres, and is generally at most about 50. Preferably, the
25 draw ratio is from 1.1 to 40, from 1.2 to 25, more preferably from 1.3 to 10, or even from 1.4 to 5.

 Preferably, the product obtained after step b) is cooled while keeping it under tension. This has the advantage that the orientation in the product obtained during fusing and stretching, on a level of fibres and on molecular level within fibres, is
30 retained better. Such tension results from, for example, winding the product into packages subsequent to preceding steps of the process.

 In the process according to the invention at least one strand in the precursor is a spun yarn made from polyolefin staple fibres, that is the spun yarn comprises at least 50 mass% of polyolefin staple fibres. In general, yarns can be made
35 of continuous filaments, staple fibres or combinations thereof. Natural fibres can be

classified in two categories: short staple fibres (cotton like, with typical staple or filament length 15-60 mm) and long staple fibres (wool like, typical staple length 40-200 mm). Synthetic fibres are first made as continuous filaments; they can be subsequently converted into staple fibres by either cutting or stretch breaking processes. Cutting
5 generally leads to a square filament distribution (all filaments having about the same length); although modified systems allow obtaining some variation in the filament length distribution. Stretch breaking generally results in staple fibres having a more Gaussian-like distribution of filament lengths. In a stretch breaking process, the filaments are stretched between several sets of rollers operating at different speeds until they break.

10 Staple fibres can be made into yarn via a process of pulling and twisting strands of parallel fibres, generally referred to as spinning. For this reason, yarn made from staple fibres is called spun yarn.

Industrial yarn spinning processes include the following basic process steps: loosening, carding, drawing and spinning. Loosening refers to separating and
15 optionally cleaning of e.g. baled staple fibres. Carding is the further loosening and separating of fibres, for example by passing them between rotating drums covered with needles. This results in a thin web of partly paralleled fibres, which is formed into a rope-like strand often called a sliver. Combing may then be applied to enhance orientation of fibres and to remove small fibres. During drawing, slivers are drawn out in
20 one or more steps. Several slivers, either of the same or of different staple fibres, may be blended together in order to obtain a uniform fibre density. Mixing staple fibres at the carding stage can also make yarns comprising blends of different natural and/or synthetic fibres. Before feeding to the spinning machine, the sliver may be further drawn while a slight twist is added, called roving. During spinning, the sliver or roving is
25 further drawn out and a twist is added to provide cohesion of the overlapping fibres, and the yarn is wound onto bobbins. Such a package of wound yarn may be of conical or cylindrical form, and is normally simply referred to as package.

The described spinning process results in a twisted, single-strand yarn, also called single yarn. Depending on the twisting direction applied, such yarns
30 are often referred to as either S or Z yarns. A twisted single-strand yarn is generally rather 'lively', meaning that it tends to twist, tangle, slant or curl round itself when held with insufficient tension. In order to reduce this liveliness, that is to obtain a calm or balanced yarn that can be satisfactorily further processed into e.g. a fabric, it has been generally accepted in industry that two or more strands of single yarns need to be
35 combined in an additional step. Such combining step is normally called folding or

plying. A two-fold yarn, or two-ply yarn can, for example, be made by twisting together two single-strand Z yarns with a S-twist, or by plying together a Z and S type yarn. The thus obtained folded yarns may also be stronger and more uniform than single-strand yarns.

5 The spun yarn applied in the process according to the invention comprises at least 50 mass% of polyolefin staple fibres. The spun yarn may further comprise up to 50 mass% of one or more other staple fibres, like natural fibres or synthetic fibres, to make a blend yarn. Suitable examples of such secondary staple fibres include wool, polyolefin, acrylic, polyester or polyamide, including aromatic
10 polyamide fibres.

 In a special embodiment of the process according to the invention, the spun yarn comprises an amount of a staple yarn made from a thermoplastic polymer having a lower melting point range than the polyolefin staple fibres. The advantage hereof is that additional thermal bonding may take place during step a). Use
15 of a spun yarn in the process according to the invention enables this possibility, since making a blended spun yarn is easier and more economical than making a blended multi-filament yarn. Examples of suitable thermoplastic polymers include copolymers of at least one alpha-olefin with other monomers, like LLDPE, or ethylene-acrylic copolymers. Effective amounts of such staple fibres can be determined by
20 experimentation, and are generally about 5 to 25 mass%.

 In a further special embodiment according to the invention, the main component of the spun yarn is not a polyolefin staple fibre, but a staple fibre made from a high strength, high modulus filament yarn having a higher heat resistance than a polyolefin and that cannot be thermally bonded per se; like an aromatic polyamid yarn
25 such as Kevlar® or Twaron®, a liquid crystalline polyester yarn, or polybenzoxazole or polybenzothiazole based yarn. Such spun yarn further comprises up to 50 mass% of a staple yarn made from a thermoplastic polymer having a relatively low melting point range, for example polyolefin staple fibres with a melting point below 200°C. Examples of suitable thermoplastic polymers include copolymers of at least one alpha-olefin with
30 other monomers, like LLDPE, or ethylene-acrylic copolymers. The advantage of this embodiment is that thermal bonding can take place during step a), whereas without the presence of fibres with low melting point no monofilament-like product can be made from such high strength, high modulus filament yarns having a high heat resistance by exposing it to heat while stretching. Effective amounts of such thermoplastic heat
35 fusable staple fibres can be determined by experimentation, and are generally about 5

to 25 mass%. A monofilament-like product based on a spun yarn comprising aromatic polyamid staple fibres and heat-fusible staple fibres made by said process combines high strength, high abrasion resistance and high thermal resistance.

5 The spun yarn, and the staple fibres, may further contain the usual additives, like stabilizers, colorants, mineral particles, sizing agents, and the like.

The choice of the other staple fibres, e.g. type, length, titre (dpf), whether they can be fused under the applied temperature and time conditions along with the polyolefin staple fibres, and/or of additives, is mainly determined by the ultimate properties that are desired, and can be made by the skilled person using
10 general knowledge or routine experimentation.

Preferably, the spun yarn that is applied in the process according to the invention comprises at least 60, 70, 80 or even 90 mass% of polyolefin staple fibres, because this enables better mechanical properties of products obtained. For this reason, the spun yarn applied most preferably comprises essentially only said staple
15 fibres.

Staple fibres obtained from various polyolefin yarns can be chosen as staple fibres for application in the process according to the invention. Particularly suitable polyolefin yarns are made from homo- and copolymers of ethylene or propylene. In addition, the polyolefins used may contain small amounts of one or more
20 other monomers, in particular other alpha-olefins. Good results are achieved if linear polyethylene (PE) is chosen as polyolefin. Linear polyethylene is here understood to be polyethylene with less than one side chain per 100 carbon atoms, and preferably less than one side chain per 300 carbon atoms; a side chain or branch usually containing at least 10 carbon atoms. The linear polyethylene may further contain up to 5 mol% of
25 one or more comonomers, such as alkenes like propylene, butene, pentene, 4-methylpentene or octene. Besides the polyolefin the fibre may contain small amounts of solvents or additives that are customary for such fibres, such as anti-oxidants, spin-finishes, thermal stabilizers, colorants, etc.

Preferably, the polyolefin fibre, in particular the polyethylene fibre,
30 has an intrinsic viscosity (IV) of more than 5 dl/g. Because of their long molecule chains, polyolefin fibres with such an IV have very good mechanical properties, such as a high tensile strength, modulus, and energy absorption at break. This is also the reason why even more preferably the polyolefin is a polyethylene with an IV of more than 10 dl/g. The IV is determined according to method PTC-179 (Hercules Inc. Rev.
35 Apr. 29, 1982) at 135°C in decalin, the dissolution time being 16 hours, the anti-oxidant

is DBPC, in an amount of 2 g/l solution, and the viscosity at different concentrations is extrapolated to zero concentration. Polyethylene of such high viscosity is often called UHMwPE. UHMwPE filament yarn can be prepared by spinning of a solution of UHMwPE into a gel fibre and drawing the fibre before, during and/or after partial or complete removal of the solvent; that is via a so-called gel-spinning process as for example described in EP 0205960 A, in WO 01/73173 A1, in Advanced fiber spinning technology, Ed. T. Nakajima, Woodhead Publ. Ltd (1994), ISBN 185573 182 7, and in references cited therein.

Preferably, UHMwPE staple fibres are chosen, because they combine high strength with a low relative density. More specifically, the spun yarn that is applied in the process according to the invention comprises UHMwPE staple fibres that have been made via a stretch-breaking process from a multi-filament UHMwPE yarn, since the broader fibre length distribution of such staple results in a yarn with better mechanical properties.

In a special embodiment, the spun yarn applied is a single-strand spun yarn. In a further embodiment, the single-strand spun yarn as described in a co-pending application, which is not yet published, is applied in the process according to the invention. This single-strand spun yarn has been made from at least 50 mass% of staple fibres that have been obtained from a continuous polyolefin multifilament yarn having a tensile strength of at least 16 cN/dtex; a tensile modulus of at least 700 cN/dtex; and a denier per filament of fibre of at most 18 dpf; which staple fibres have an average fibre length of between 40 and 180 mm; and show essentially no crimp; and which spun yarn has a twist level characterized by an α twist coefficient of 40 -100 $\text{t.m}^{-1} \cdot (\text{m/g})^{-1/2}$. Preferably, the staple fibres have been obtained from highly-oriented polyolefin fibres, such as those based on ultra-high molar mass polyethylene (UHMwPE). The advantage of this process is that translucent or semi-transparent monofilament-like products having a relatively low titre, e.g. of 10-100, preferably 15-50 dTex, and a low relative density can be made at higher overall production rate and lower overall costs compared with the process known from EP 0740002 A1 starting from multi-filament yarns. The products obtained by this process are especially suited for medical applications, like surgical sutures.

The α twist coefficient characterizes the twist level of a yarn according to the Koechlin equation: $T = \alpha (\text{Nm})^{1/2}$, wherein T is the twist level expressed as the number of turns per meter (t.m^{-1}) and Nm is the metric yarn count

(1000/tex, or m/g). This twist coefficient is also referred to as (metric) twist factor, or twist multiplier; see for example at <http://www.fibre2fashion.com/GLOSSARY/glossary17.htm>. Preferably, the twist coefficient is between 60 and 100, 65 and 90, or even between 70 and 85.

- 5 This single-strand spun yarn shows very little liveliness, and is calm enough to enable further processing without the need of first making a folded yarn. The staple fibres in the single-strand spun yarn have been obtained from a filament yarn having a linear density of at most 18 denier per filament (dpf), preferably at most 14, more preferably at most 10 dpf, and even more preferred at most 6, or at most 4 dpf.
- 10 The lower the linear density of the fibres, the thinner the spun yarn can be, since a certain minimum number of fibres is needed in a cross-section to give a yarn of sufficient integrity. Furthermore, a lower the linear density of the fibres results in higher tensile strength of the spun yarn at a constant yarn titre. In view of fibre production efficiency it is preferred that the linear density is at least 0.2, 0.3 or at least 0.5 dpf.
- 15 Starting from thinner spun yarns has the advantage that thinner monofilament-like products can be produced in a more economical way.

- The single-strand spun yarn applied in the process according to the invention comprises polyolefin staple fibres that show essentially no crimp; the fibres not being, or only slightly textured. Crimp is a measure for the waviness of a fibre, and
- 20 may be expressed as the difference between the length of the straightened or fully extended fibre and the crimped length, that is the length of the fibre when substantially free from external restraint. Showing essentially no crimp is herein understood to mean that the length of the staple fibres in unstrained condition is at least 80% of the straightened length. Preferably, the crimped length is at least 90% of the straightened
- 25 length, even better at least 95%. Showing essentially no crimp is further understood to include no permanent crimp. For example, UHMwPE staple fibres may show some crimp that may have been introduced during staple making, but this crimp is not permanent, since it will essentially disappear upon exposing the fibres to elongational forces, which may e.g. occur during spinning.

- 30 In the process according to the invention at least one strand in the precursor is a spun yarn made from polyolefin staple fibres. The precursor may also contain one or more strands made from other staple fibres and/or from continuous filaments, to arrive at a monofilament-like product of different degrees of fusion between and within strands and at different mechanical properties and appearance and
- 35 feel. Such variations can be made by a skilled person using general knowledge or

routine experimentation. Preferably, all strands in the precursor are spun yarns based on polyolefin staple fibres, since this allows to vary the degree of fusion, and thus of product properties to a great extent.

The process according to the invention can be performed with a precursor of various constructions, for example of a braided construction, or a plied and twisted construction. Preferably, a precursor with plied (or folded) and twisted strands is applied. This has the advantage that the precursor can be made more easily and more cost-effectively; and that the product obtained shows better performance; especially surprisingly good resistance to failure during abrasion tests.

The process according to the invention can further comprise a step preceding step a) of pretreating the precursor, or one or more of the strands therein, in order to enhance inter fibre bonding during the fusion step. Such pre-treatment step may include coating the precursor with a component or a composition; scouring the precursor, that is washing-off surface components like spin finishes etc.; or applying a high-voltage plasma or corona treatment.

In one embodiment the precursor is pretreated by applying; e.g. by dipping or wetting, an effective amount of a mineral oil (e.g. heat transfer grade mineral oil with an average molar mass of about 250-700), vegetable oil (e.g. coconut oil), or a, preferably non-volatile, solvent for polyolefin, like paraffin. This pre-treatment step may be performed at ambient conditions, or at elevated temperature up to below the melting temperature range of the polyolefin fibre.

In another embodiment, pretreating comprises applying a coating composition to the precursor, which composition may be a solution or dispersion of a polymer that enhances fibre to fibre bonding during exposure to higher temperature at the fusing step, or otherwise improves performance. In a preferred embodiment, the precursor is coated with a polyurethane composition, like a dispersion of film-forming polyurethane. Such a composition may further comprise components that contribute to improving the abrasion- or cut-resistance of the monofilament-like product. Examples of components that improve cut-resistant are small particulate particles of high surface hardness, like mineral particles, ceramic particles, glass, metals and the like. The coating composition may further comprise other additives, like colorants or stabilisers.

The process according to the invention can further comprise a step wherein a coating composition is applied to the product after steps a) and b) to form a coating layer. Such coating composition may comprise a typical spin finish to allow easier handling and processing of the product in subsequent operations; a compound

or composition to control adhesion during subsequent making of composite articles comprising the product; or a binder composition that further enhances integrity and strength of the product. Typical examples of the latter include polyurethane or polyolefin-based, like ethylene-acrylic copolymers, binder compositions. The coating
5 composition may be applied as a solution or dispersion. Such a composition may further comprise components that further improve the abrasion- or cut-resistance of the monofilament-like product. Examples of components that improve cut-resistant are small particulate particles of high surface hardness, like various mineral or ceramic particles. The coating composition may further comprise other additives, like colorants,
10 stabilisers, etc.

Application of a coating composition in the process according to the invention is found to be relatively easy and effective compared with a process wherein continuous filament yarn is applied as precursor. Apparently the product obtained after steps a) and b) is more receptive towards such coatings, especially if the fibres at the
15 surface of the product have been only partly fused.

The invention also relates to a monofilament-like product comprising an at least partly fused spun yarn made from polyolefin staple fibres, which product is obtainable by the process according to the invention. This product has a unique structure and combines several advantageous properties; it has the translucent
20 appearance of a monofilament, yet its touch and feel are different from polyolefin monofilaments or monofilament-like products as known from, for example, EP 0740002 B1. The monofilament-like product according to the invention shows surprisingly high resistance to break during abrasive testing; can be easily knotted, and the knotted product shows high retention of strength. The monofilament-like product
25 also shows surprisingly high tensile strength; even significantly higher than the strength of the starting spun yarn in the precursor. Typically, the monofilament-like product has a tensile strength of at least 10 cN/dtex, preferably at least 15, 20 or even 25 cN/dTex. Such a high strength is typically found for a product based on a precursor that comprises a relatively high amount of spun yarn based on UHMwPE staple fibres.

30 The monofilament-like product obtainable by the process according to the invention has a linear density, also referred to as titre, which may vary within wide limits, e.g. from 10 to 15000 dTex. Generally, the product has a titre of from 30 to 2500 dtex. The lower titre products are suitable for use as sutures and the like. In view of applications like fishing lines, or protective garments and clothing, the titre is
35 preferably from 100 to 1600 dTex, even more preferably from 200 to 1200 dTex.

The invention further relates to the use of the monofilament-like product according to invention for making various semi-finished and end-use products, like fishing-lines; sutures, fabrics; cords and ropes; composite yarns; and their use in for example cut-resistant articles.

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The invention also concerns semi-finished and end-use products comprising the monofilament-like product according to the invention.

The invention will now be further illustrated by the following examples and comparative experiments.

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Materials and methods

Multi-filament UHMwPE yarn, Dyneema® 1760SK60 (DSM High Performance Fibres, NL), having a titre of 1760 dTex, a tensile strength of 28 cN/dTex, a tensile modulus of 910 cN/dTex, and a denier per filament of fibre of about 1 dpf was made into staple fibres by a stretch-breaking process, as for example described in EP 0445872 A1. The average length of the staple fibres was about 80 mm. The staple fibres were subsequently spun into a single-strand yarn using NSC equipment of the long staple fibre type. The yarn obtained had a yarn count of about Nm 44 (about 225 dTex), the twist level applied corresponded to at coefficient of about 80 Koechlin law). The spun yarn showed little liveliness, as was demonstrated by cutting a length of 100 cm, holding it vertically fixed at only one end, and observing hardly any tendency to twist. Its tensile strength was about 15.0 cN/dTex, tensile modulus about 153 cN/dTex, and elongation at break about 4.3%. This material is referred to as SSSY hereafter.

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The tensile strength (or strength) (and the tensile modulus) are defined and determined on multifilament and spun yarns, and on monofilament-like products as specified in ASTM D885M, using a nominal gauge length of the fibre of 500 mm, a crosshead speed of 50%/min and Instron 2714 clamps. For calculation of the strength, the tensile forces measured are divided by the titre, as determined by weighing 10 metres (or another length) of fibre. Elongation is the measured elongation at break, expressed in % of the original length after clamping the specimen.

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Knot strength is determined by measuring the strength of a specimen comprising a Palomar-knot. The Palomar-knot is a general-purpose connection recommended for joining a fishing line to a swivel, a snap or a hook. The doubled end of the specimen is passed through the eye of a hook and a simple overhand knot is made. The hook is then passed through the loop and the knot is tightened.

Knot strength efficiency is calculated as the relative value (%) of the measured knot strength to measured tensile strength.

Abrasion resistance was measured following a procedure based on the test described by ASTM D 3108 for determining yarn friction. For this purpose the Yarn Friction Measuring Apparatus described in ASTM D 3108 has been adapted, such that one end of the sample to be tested is fixed to an eccentric crank or cam rotated by a motor, the other end is loaded with a weight. During the test the sample is abraded against a ceramic eye and the number of cycles is determined until the sample fails (breaks). The number given is the average of at least 5 tests.

Comparative experiment A

As precursor (feed) material a braided construction made from a multi-filament gel-spun UHMwPE yarn having a titre of 224 dTex, a tensile strength of 39 cN/dTex, a tensile modulus of 1250 cN/dTex, and a denier per filament of fibre of about 1 dpf was applied. This braid contained 8 strands of said yarn braided with a medium tightness, expressed as picks per centimetre, of 7.5 (presented as 8 x 224 / 7.5; see Table 1).

This braid was passed through a bath of liquid paraffin as pretreatment step, and excess oil was wiped off by passing between non-woven fabrics. The paraffin content was calculated to be about 11 mass% by determining the mass increase upon this step. The braid was then guided over first driven rolls into an oven, kept at a constant temperature of 153.5°C, with a constant speed of 10 m/min. At the exit of the oven, the braid was guided over second driven rolls. The speed of the second rolls was adjusted such that a draw ratio of 1.9 and a stretch rate of 0.7 m/min was applied. In case a different draw ratio is to be applied, as in some other experiments, the stretch rate in the oven is kept about constant by varying the pathlength of the sample in the oven and the speed of the second rolls. The oven is equipped with a number of rolls, such that the sample pathlength in the oven can be from 2.8 upto 58.8 meter.

The product appearance changed from initially opaque white to almost translucent; its surface was still rather smooth, although definitely less smooth and shiny than of the starting product. Also the product felt more rough and stiffer, and retained at an angle after bending.

Results of further testing are compiled in Table 1. It should be noted that the knot strength efficiency found is markedly lower than reported for similar

products in EP 0740002 B1; this may be related to the type of knot that is used.

Comparative experiment B

5 The experiment was performed largely analogous to Comp. Exp. A, be it that a twisted and plied construction was made from 6 strands of the same multifilament yarn, applying a clockwise twist of 120 turns/cm (indicated as 6 / 224; 120Z). Measured paraffin content was about 12 mass%; the draw ratio was 1.8. Results of further testing are compiled in Table 1.

10 Example 1

 A braided construction containing 8 strands of the SSSY material described above, with 12 picks/cm (indicated as 8 x Nm44 / 12 in Table 1) was used as precursor. Analogously to Comp. Exp. A this braid was passed through the oven, but without any pre-treatment step and applying a draw ratio of 1.0. The resulting product
15 had similar appearance as its starting material; it was found to have a lower tensile strength than the spun yarn originally applied as strands. The product showed high strength retention after a knot was made.

Examples 2-3

20 Example 1 was repeated, but now about 12 mass% paraffin was added before step a) and a draw ratio of 1.8, respectively 1.7, was applied. The more translucent appearance of the products indicates more fusion to have taken place. The surface touch was less smooth than for Comp. Exp. A. Both resulting products have a higher tensile strength than the spun yarn applied as strands, show a higher resistance
25 to bending (stiffer) and retain at an angle after bending. The number of cycles until break during abrasion testing was found to be more than 5 times higher for Ex. 2 than for Comp. Exp. A.

Examples 4-6

30 Braided constructions made from the SSSY material described above, containing 8 strands with 9.5 picks/cm were used as precursor. Analogously to Comp. Exp. A, this braid was passed through the oven, but without any pre-treatment step and applying a draw ratio of 1.0. The resulting product appeared to have a lower tensile strength than the spun yarn applied as strands; but a knot could but made with
35 high strength retention (Ex. 4). If a draw ratio of 1.6 or 1.7 was applied, the tensile

strength again increased, as with Ex. 2-3; but the abrasion resistance was only slightly better. Apparently under the temperature and time conditions applied, the degree of fusion of the fibres was not high enough to result in high abrasion resistance, without a pre-treatment.

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Examples 7-9

Examples 4-6 were repeated, but now about 13 mass% of paraffin was added to the precursor. A strength increase vs. the original spun yarn was observed for all samples; example 7 confirms the positive effects of a higher degree of fusion on abrasion resistance.

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Examples 10-16

Braided constructions made from the SSSY material described above, containing 8 strands with 7.5 picks/cm were used as precursor. Ex. 10 confirmed that at draw ratio 1.0 no increase in tensile strength is found; and that without pre-treatment and under the chosen conditions only little fusing occurs. Adding paraffin and increasing exposure temperature increases degree of fusion, as judged from appearance change. Improved fusion was also apparent from testing resistance to desintegration of the product upon abrading it over a metal rod; Ex. 11 could withstand 18, Ex. 12 and 13 about 33 movements. A 4-5 fold increase was observed in the number of cycles until break in the abrasion resistance test. A higher temperature or draw ratio did not result in further improvement in tensile properties for the present precursor construction.

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Example 17

The single-strand spun yarn SSSY was used as precursor. Pretreatment consisted of applying an aqueous polyurethane dispersion, L9010 ex GOVI (BE), via dipping. The polyurethane content was determined (on the resulting product) to be about 15 mass%. The combination of pre-treatment, heat exposure and stretching with draw ratio 1.6 markedly increased tensile strength of the product. The product also had higher stiffness, more translucent appearance, and a knot could be made easily with high strength retention.

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Examples 18-22

As precursor a 6-fold yarn based on SSSY, having a clockwise twist

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of 120 turns/cm (indicated as 6 / Nm₄₄; 120Z) was applied. In Ex. 19 about 13.5 mass% of paraffin was added as pre-treatment, combined with a draw ratio of 1.8. This fused product showed very good resistance to break during abrasion testing; about 15-fold increase vs. Comp. Exp. B. The samples made with a polyurethane pre-treatment (Ex. 20-22; PUR content about 16 mass%) showed very good tensile properties and knot strength (efficiency), and improved abrasion resistance.

Examples 23-24

The products were based on an 18-fold, twisted yarn (starting strands were SSSY), with about 12.5 mass% paraffin and were made under analogous conditions as before. The results obtained for these thicker products, with titres of about 4100 and 2500 dTex, respectively, are in line with the other results.

Table 1

Precursor material		Process characteristics			Product properties				
Type	construction	Pre-treatment	Temp. (°C)	Draw ratio	Tensile strength (cN/dTex)	Elongation (%)	Knot strength (cN/dTex)	Knot strength efficiency (%)	Abrasion resistance (cycles until break)
Comp. Exp. A	Braided; cont. filament yarn	paraffin	153.5	1.9	27.9	3.8	15.2	54	5998
Ex. 1	Braided	none	153.5	1.0	10.8	6.0	8.1	75	
Ex. 2	Braided	paraffin	153.5	1.8	17.2	2.1	9.2	54	32998
Ex. 3	Braided	paraffin	153.5	1.7	16.5	2.1			
Ex. 4	braided	none	153.5	1.0	12.9	4.5	10.5	81	
Ex. 5	braided	none	153.5	1.6	22.4	2.8	14.9	67	7828
Ex. 6	braided	none	153.5	1.7	22.2	2.5			
Ex. 7	braided	paraffin	153.5	1.6	20.2	2.5			25171
Ex. 8	braided	paraffin	153.5	1.7	16.7	2.0			
Ex. 9	braided	paraffin	153.5	1.8	18.5	2.0			
Ex. 10	braided	none	153.5	1.0	11.5	4.4			
Ex. 11	braided	paraffin	153.5	1.6	20.1	2.5	11.9	59	26234
Ex. 12	braided	paraffin	154.0	1.6	18.1	2.7			
Ex. 13	braided	paraffin	154.5	1.6	17.1	2.4			30620
Ex. 14	braided	paraffin	155.0	1.6	16.8	2.7			

Precursor material		Process characteristics				Product properties			
Type	construction	Pre-treatment	Temp. (°C)	Draw ratio	Tensile strength (cN/dTex)	Elongation (%)	Knot strength (cN/dTex)	Knot strength efficiency (%)	Abrasion resistance (cycles until break)
Ex. 15	braided	paraffin	153.5	1.7	19.8	2.2			
Ex. 16	braided	paraffin	153.5	1.8	18.6	2.1			
Comp. Exp B	Plied and twisted cont.filament yarn	paraffin	153.5	1.8	29.4	3.9	17.5	60	6868
Ex. 17	Single spun yarn	PUR	153.5	1.6	21.4	2.1	17.1	80	
Ex. 18	Plied; twisted	none	153.5	1.0	14.8	4.0			
Ex. 19	Plied; twisted	paraffin	153.5	1.8	18.5	2.2	15.2	82	>100000
Ex. 20	Plied; twisted	PUR	153.5	1.6	23.8	2.5			
Ex. 21	Plied; twisted	PUR	153.5	1.7	27.3	2.9	21.5	79	24580
Ex. 22	Plied; twisted	PUR	153.5	1.8	24.1	2.5			
Ex. 23	Plied; twisted	none	153.5	1.0	14.5	4.8			
Ex. 24	Plied; twisted	paraffin	153.5	1.6	19.1	2.8			